

INORGANIC FORMATION OF ZONED Mg-Fe-Ca CARBONATE GLOBULES WITH MAGNETITE AND SULFIDE RIMS SIMILAR TO THOSE IN MARTIAN METEORITE ALH84001. D. C. Golden¹, D. W. Ming², C. S. Schwandt³, H. V. Lauer³, R. A. Socki³, R. V. Morris², G. E. Lofgren², and G. A. McKay², ¹Hernandez Engineering Inc. 17625 El-Camino Real, Suite 200, Houston, TX 77058 d.c.golden1@jsc.nasa.gov, ²SN-2, NASA-JSC, Houston, TX 77058, ³Lockheed Martin Corp., Houston, TX 77058.

Introduction: Martian meteorite ALH84001 has been the focus of intense research since D. McKay et al. [1] suggested that certain mineral assemblages (i.e., carbonate globules, magnetites, and Fe-sulfides) and polycyclic aromatic hydrocarbons (PAHs) in ALH84001 are evidence for ancient Martian life. The origin of the carbonates, magnetites and Fe-sulfides in ALH84001 is controversial. The controversy centers around (i) the formation temperature of the carbonates with low temperatures required for biogenic processes and (ii) whether the unique properties of the carbonates (e.g., compositional zoning), magnetites (single domain and parallelepiped morphology), and sulfides can be formed only by biogenic processes.

Although numerous researchers have suggested inorganic processes for the formation of the zoned carbonates, magnetites, and sulfides, few experiments have been done to replicate the globules and place constraints upon their conditions of formation. We recently synthesized spherical Mg-Fe-Ca-carbonates from Mg-Fe-Ca-CO₂-H₂O solutions under mild hydrothermal conditions that have similar carbonate compositional zonation to those of ALH84001 [2]. These synthetic carbonates have an ankerite core grading into a magnesite-rich rim. However, we were unable to reproduce the zoning sequence of carbonates, magnetites and sulfides similar to those in ALH84001 from a one-step hydrothermal, batch precipitation procedure. Based upon the history of ALH84001, it is possible that the unique zonation sequence in its carbonate globules is a multi-step process, including precipitation from multiple influxes of solutions having different compositions (or a single solution influx with varying composition) and heating due to shock events. We show here experimental evidence that the carbonate-sulfide-magnetite assemblage in ALH84001 may result from a multi-step inorganic process.

Synthesis Procedure: ALH84001-like carbonates were prepared by using a procedure modified from Golden et al. [2]. Bicarbonate solutions were placed into TeflonTM-lined reaction vessels and heated to 150°C. Under these conditions, the bicarbonate decomposed followed by the precipitation of carbonates. Compositional zonation in the carbonate was achieved by changing solution compositions in a four step procedure (Table 1). At the end of the 4th step, the product was washed free of soluble salts and freeze-dried. To simulate heating from a shock event, freeze-dried samples were heated to 470°C in a Perkin

Elmer differential scanning calorimetry (DSC) apparatus at 20°C/min in a stream of CO₂ at 100 Torr and cooled immediately at 20°C/min. Products were characterized by x-ray diffraction (XRD) analysis and electron beam analytical techniques.

Results: The XRD mineralogy of carbonate globules following solution precipitation and freeze-drying (not heated to 470°C) was ankerite, siderite, pyrite, magnetite, and magnesite. From core to rim, the globules were zoned in the sequence from ankerite to siderite+pyrite, to magnesite, to siderite+pyrite rim (data not shown). Each of these zones represents the major precipitation products from the corresponding synthesis step described in Table 1. In the sample heated to 470°C, XRD mineralogy of synthetic globules was ankerite, magnetite, pyrrhotite, and magnesite. The elemental distribution of these synthetic globules resembles that of carbonate globules in ALH84001 (Fig. 1). Calcium and Fe are concentrated in the central area of the core, which becomes more Mg-rich near the first magnetite+pyrrhotite zone. The two magnetite+pyrrhotite zones are evident from the high Fe and S areas near the outer edges of globules (EDS line scans not shown). A very-well defined Mg-rich zone (magnesite) lies between the inner magnetite+pyrrhotite zone and the outer magnetite+pyrrhotite rim.

Globules ranged from 10 to 80 µm in diameter. Globules that formed in the cracks of orthopyroxene crystals (data not shown) had a “pancake-shaped” morphology, similar to that reported for ALH84001 globules [1].

Magnetites were produced by two processes: precipitation from solution (small population of the total magnetites) and as decomposition products of siderite during heating to 470°C (majority of magnetites). Precipitated magnetites were hexagonal plates, cubes, and parallelepipeds and occurred in the 10-1000 nm size range. Magnetites that formed during siderite decomposition had irregular, parallelepiped, or tooth-shaped morphologies, were fairly uniform in size (10-100 nm), and fall into the single domain size range [3].

The relationship of the magnetites, carbonates, and sulfides near the globule rim is illustrated by the

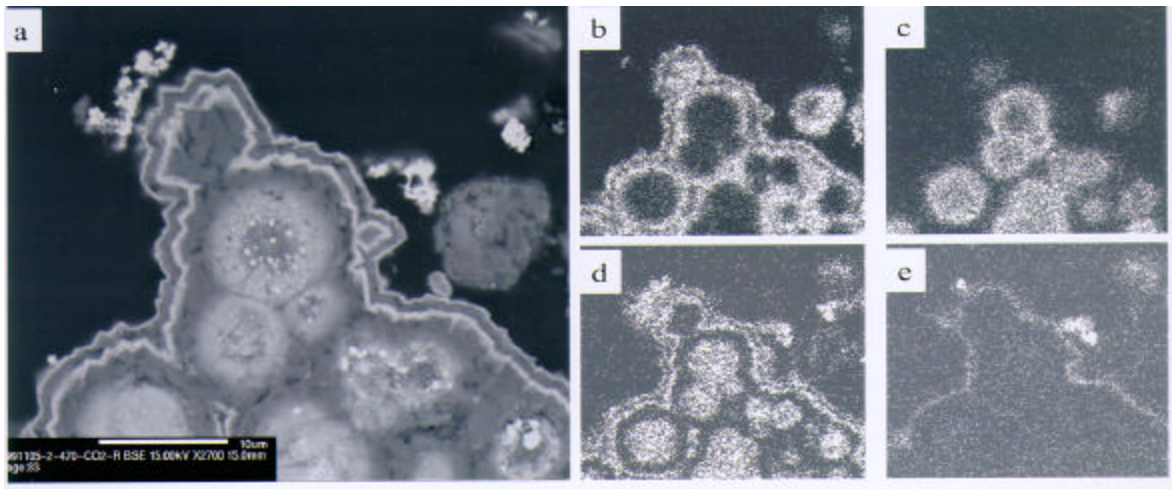


Figure 1. Scanning electron micrographs of zoned carbonate globules formed by precipitation from solution followed by heating (470°C) (a) Backscattered-electron image (b) Mg X-ray map (c) Ca X-ray map, (d) Fe X-ray map and (e) S X-ray map.

transmission electron microscopy image in Figure 2. The Mg-rich carbonates are fractured during the thin sectioning by the diamond knife; however, the magnetite and sulfide bands are very prominent. Magnetites that formed by siderite decomposition are chemically pure and free of lattice defects.

Discussion: The carbonate formation process in the ALH84001 may have occurred inorganically as sequential aqueous precipitation in the fractured host rock. A heating event, probably associated with a impact event, converted the siderite to magnetite and the pyrite to pyrrhotite. The temperature of the heating event was such that only the siderite decomposed and ankerite and magnesite remained mostly unchanged. We have constrained the upper temperature of this heating event to be $\approx 500^{\circ}\text{C}$ (atmospheric pressure and composition dependent), based upon the thermal properties of the synthetic siderite, ankerite, and magnesite as determined by differential scanning calorimetry and XRD analyses. Our observations are consistent with petrographic data presented by Brearley [4], who suggested that the single-domain magnetites in ALH84001 formed by the decomposition of the siderite following shock melting of plagioclase-rich glass associated with carbonate globules. However, unlike Brearley’s observations, nearly all the magnetite morphologies found in ALH84001 have been experimentally produced in our study.

Our experimental studies show that it is possible to synthesize carbonate globules quite similar to those of ALH84001 by simple inorganic processes that may have occurred on early Mars.

References: [1] McKay D. S. *et al.* (1996) *Science* **273**, 924. [2] Golden D. C. *et al.* (2000) *Meteor. & Planet. Sci.*, in press. [3] Butler R. F. & Banerjee S.K. (1975) *J. Geophys. Res.* **80**, 4049. [4] Brearley A. J. (1998), *Lunar & Planet. Sci.*, 29, CD-ROM.

Table 1. Experimental conditions and procedure for the synthesis of carbonate globules.

	Conditions						
	Solution Compositions					Vol	Time
	Ca	Fe	Mg	NaHCO ₃	S		
	-----mMoles-----					mL	h
Step 1	0.45	0.3	1.8	3		15	7
Step 2	0	1.5	0	1.5	0.16	15	1
Step 3	0	0	1.8	3.75		15	10
Step 4	0	1.5	0	1.5	0.16	15	1
Step 5	Heat at 20°C/min to 470°C in CO ₂ at 100 Torr						

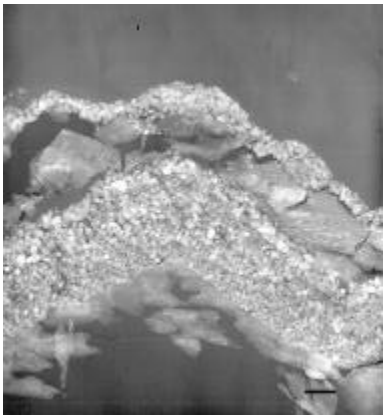


Figure 2. Transmission electron micrograph of thin-sectioned carbonate globule rim formed by precipitation followed by heating (470°C). Note the narrow size distribution of magnetites formed by decomposition of siderite (bar = 200 nm).